Layering in ionic liquids

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Layering is the arrangement of molecules or ions into discrete layers adjacent to a smooth solid surface. Layering of room temperature ionic liquids (ILs) has been reported in literature [1, 2] and causes thin films of ILs to behave as if they were solid. This has profound effects: nanoparticles dispersed in thin films of IL can be investigated by Transmission Electron Microscopy (TEM) without Brownian motion blurring the image (Fig. 1). Also holes with controlled size and shape can be written into thin films of ILs by means of Focused Ion Beam (FIB). In figure 2 the letter *M* has been written in a film of IL, suspended in a holey carbon grid. Effects can be noticed in electrodeposition as well: figure 3 shows an electrodeposited layer of copper. Some copper grains are separated by a thin gap, as indicated by the arrows. It is believed that between the grains, the IL acts as a solid, thereby hindering the coalescence of the grains.

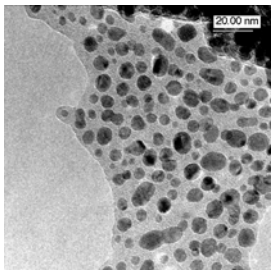

Figure 1

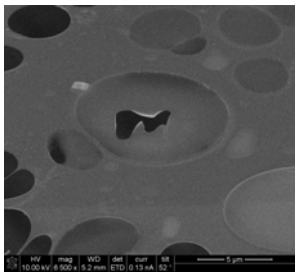

Figure 2

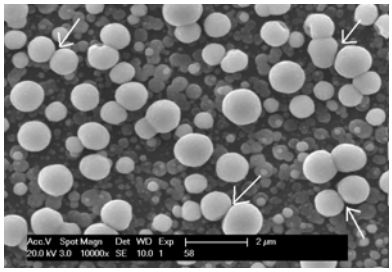

Figure 3

As a result of the layering effect, the solvation force normal to the interface shows an oscillating behavior which can be measured by AFM force microscopy. AFM measurements were performed on [1-butyl-1-methylpyrrolidinium][bis(trifluoromethyl-sulfonyl)imide], [1-butyl-3-methylimidazolium][tetrafluoroborate] and [1-decyl-3-methylimidazolium][tetrafluoroborate] and their mixtures. In all tested ILs, layering was detected. Both the amount of layers and thickness of the layers vary in different ionic liquids since the size of the anions and cations are different. The presence of copper(II) ions increases the number of layers, especially for longer alkyl chains on the imidazolium IL. The influence of electrochemical polarization on layering was also investigated.

1. R. Atkin and G.G. Warr, J. Phys. Chem. C, **2007**, 111 (13), 5162-5168
2. D. Wakeham, R. Hayes, G.G Warr and R. Atkin, J. Phys. Chem. B, **2009**, 113 (17) 5961-5966